



Cite this: *Soft Matter*, 2015, 11, 5180

# Photophysical and photochemical processes in 3D self-assembled gels as confined microenvironments

Raúl Pérez-Ruiz†<sup>\*a</sup> and David Díaz Díaz†<sup>\*ab</sup>

Received 14th April 2015,  
Accepted 5th June 2015

DOI: 10.1039/c5sm00877h

www.rsc.org/softmatter

Numerous challenging transformations take place in nature with high efficiency within confined and compartmented environments. This has inspired scientists to develop spatially micro- and nanoreactors by 'bottom-up' approaches in order to improve different processes in comparison to solution, in terms of kinetics, selectivity or processability. In this respect, investigation of photophysical and photochemical processes in soft gel materials has recently emerged as a new and promising research field oriented towards expanding their applications in important areas such as photovoltaics, photocatalysis and phototherapy. Herein, we summarize the few examples dealing with intragel photo-induced physical and chemical processes involving embedded reactants that do not participate in the assembly of the gel network.

<sup>a</sup> Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93040 Regensburg, Germany. E-mail: Raul.Perez-Ruiz@chemie.uni-regensburg.de, David.Diaz@chemie.uni-regensburg.de; Fax: +49 941 9434121; Tel: +49 941 9434373

<sup>b</sup> IQAC-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

† Both authors contributed equally to this work.

## Introduction

In nature, a large number of challenging chemical transformations take place in confined environments such as enzymes and cells. Over the past few decades, this has inspired scientists to develop spatially confined micro- and nanoreactors by



**Raúl Pérez-Ruiz**

*Dr Raúl Pérez Ruiz (born 1976, Valencia) obtained his BSc in chemistry at the University of Valencia (2001). In 2006, he received his PhD in chemistry with honors under the guidance of Prof. Miguel Angel Miranda at the Technical University of Valencia (UPV). After six months at the University of Athens (Greece) as post-doc (2006–2007), he was working as a postdoctoral scientist with Prof. Axel G. Griesbeck at the University of Cologne*

*(2007–2008). He rejoined to the Department of Chemistry at UPV with a postdoctoral position under the supervision of Prof. María Consuelo Jiménez (2009–2014). Currently, he is developing his scientific career at the University of Regensburg as experience postdoctoral researcher. He is the recipient of the Alexander von Humboldt Fellowship Award, Juan de la Cierva Fellowship and IEF Marie Curie Fellowship. His actual research is focused on organic photochemical processes and molecular spectroscopy.*



**David Díaz Díaz**

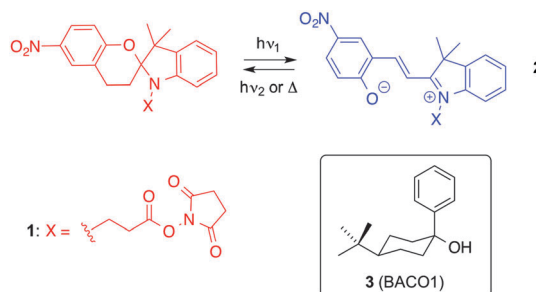
*Prof. Dr David Díaz Díaz (born 1974, Tenerife) received his PhD in chemistry with honors under the supervision of Prof. Víctor S. Martín at the University of La Laguna. In 2002, he joined Prof. Finn's group as postdoc at The Scripps Research Institute (San Diego, US). Since 2006, he has held various positions in academia and industry ('Ramón y Cajal' Researcher, Autonomous University of Madrid (UAM), Spain, 2006; Sr. Chemist, The*

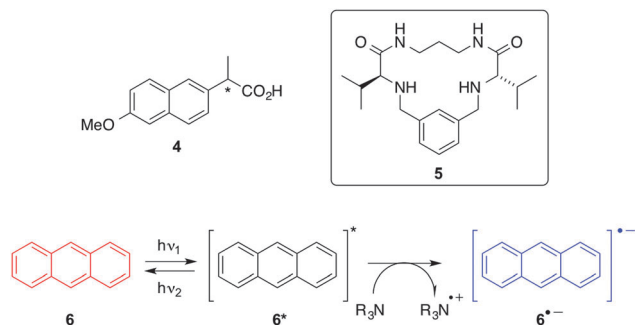
*Dow Chemical Company, Switzerland, 2007; Tenured Scientist, CSIC, Spain, 2009; Alexander von Humboldt Experienced Researcher, University of Regensburg, Germany, 2010). In 2013, he was named recipient of the prestigious DFG Heisenberg Professorship. Among several international awards, he has received the Young Investigator Award from the Polymer Network Group (Japan, 2014) and is Editor-in-Chief of Gels. His main research interest focuses on the development of advanced functional soft materials.*



Herein, we discuss a growing research area focused on the use of fibrillar gel matrices as versatile reaction vessels to carry out photophysical and photochemical processes of physically embedded reactants, giving similar or superior results than those obtained in solution state. Well-known photopolymerization of gels containing polymerizable groups<sup>16</sup> and the use of gelator systems with intrinsic photoactivity<sup>19</sup> (*e.g.*, chromophoric gelators<sup>20</sup>) are out of the scope of this manuscript.

More recently, the same group<sup>24</sup> used the LMW gelator 5 as a matrix to embed CdSe/ZnS quantum dots (QDs) with consequent fluorescence induction but without detriment of the thermal and optical properties of the parent gel. Very interestingly, the presence of the QDs decreased the critical gelation concentration

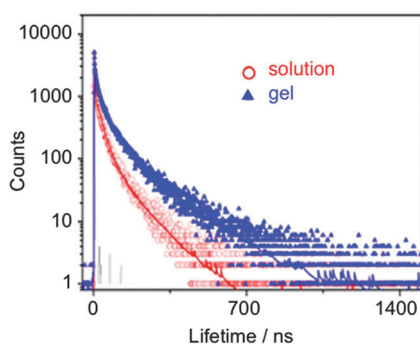
Soft Matter, 2015, **11**, 5180–5187 | 5181



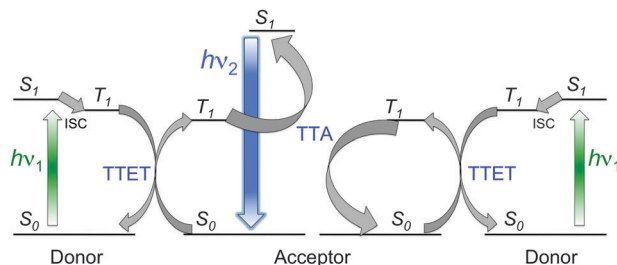
**Scheme 2** Structures of naproxen (**4**), peptidomimetic organogelator **5**, anthracene (**6**) and reduction of its excited state by amines.<sup>22</sup>

necessary to form stable organogels. A full photophysical study highlighted a remarkable example of organogel-nanoparticle symbiosis. Thus, core-shell QDs maintained their photophysical properties in the gel medium (regardless the gelator concentration), whereas a significant increase of the fluorescence intensity (*i.e.*, up to 528%) and the average lifetime (*i.e.*, up to 1.7) was observed for the core QDs embedded in the gel (Scheme 3). Moreover, some of these composites have shown fluorescence sensitivity towards nitric oxide ranging from 0.05 to 0.5 (vol%) without disruption of the semi-solid state of the supramolecular gel.<sup>25</sup>

On the other hand, photon upconversion (UC) based on triplet-triplet annihilation (TTA) between organic molecules is one of the most attractive wavelength conversion technologies, which can be performed with low-intensity and non-coherent light, such as ambient sunlight.<sup>26</sup> This phenomenon, TTA-UC, implies the association of multistep photochemical events (Scheme 4). After absorption of low energy photons ( $h\nu_1$ ), triplet excited state ( $T_1$ ) of the donor (sensitizer) is produced by intersystem crossing (ISC) from the singlet excited state ( $S_1$ ). Subsequently, triplets of the acceptor (emitter) are populated by triplet-triplet energy transfer (TTET) from the triplets of the donor (Dexter mechanism). When two acceptor molecules in their triplet states are capable to collide during their lifetimes, a higher singlet energy level is formed by triplet-triplet annihilation (TTA) and, consequently generates delayed upconverted fluorescence ( $h\nu_2$ ). This conversion of low power energy light into higher energy has been successfully applied in diverse



**Scheme 3** Fluorescence decay curves of QDs in toluene and toluene organogel containing **5** ( $3.2 \text{ g L}^{-1}$ ;  $\lambda_{\text{em}} = 530 \text{ nm}$ ). Adapted with permission from ref. 24. Copyright © 2015 American Chemical Society.

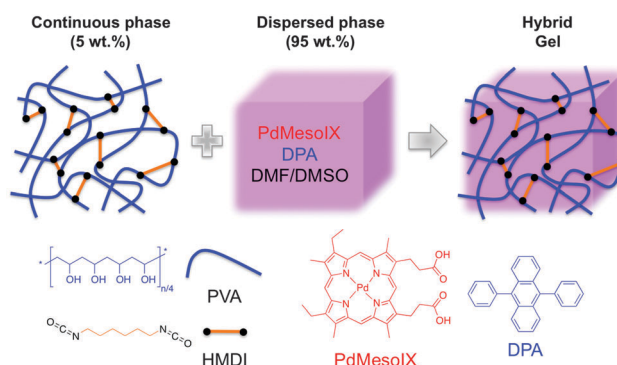


**Scheme 4** Outline of the TTA-UC process showing the involved energy levels. Adapted with permission from ref. 33. Copyright © 2015 American Chemical Society.

scientific areas such as photovoltaics, photocatalysis, bioimaging or phototherapy.<sup>27–30</sup>

It is well assumed that the best efficient TTA-UC systems have been performed in homogenous solutions due to fast diffusion of excited molecules. Within this context, the development of easily processable materials such as viscoelastic gels (*i.e.*, where liquid molecules are trapped in the interstices of fibrillar networks) that could be as efficient as a liquid composition remains a big challenge and it would provide new research areas in terms of applicability. In a seminal work, Simon and co-workers have recently developed new hybrid organogels containing the UC chromophore pair Pd(II) mesoporphyrin IX (PdMesoIX) and 9,10-diphenylanthracene (DPA) using DMF-DMSO as solvent system. In this case, the 3D polymer gel network was formed by covalently cross-linking poly(vinyl alcohol) (PVA) with hexamethylene diisocyanate (HMDI) (Scheme 5). The results demonstrated that these gels displayed an efficient green-to-blue UC with UC quantum yields of >0.6 and 14% under ambient and oxygen-free conditions, respectively.<sup>31</sup>

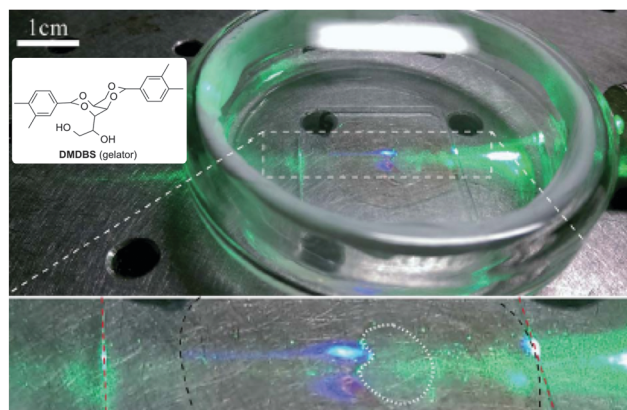
This background could be easily extended to other materials based on other solvents, gel networks (*i.e.*, chemical or physical gels) and/or chromophore pairs. Thus, Schmidt and co-workers have also published a highly efficient photochemical UC in a quasi-solid physical organogel based on 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) as LMW gelator, tetralin as solvent, and the pair palladium tetraphenylporphyrin and DPA as photochemically active compounds.<sup>32</sup> The experimental results



**Scheme 5** Graphic representation of the composition of UC hybrid organogels used by Simon and co-workers. Adapted with permission from ref. 31. Copyright © 2015 Royal Chemical Society.



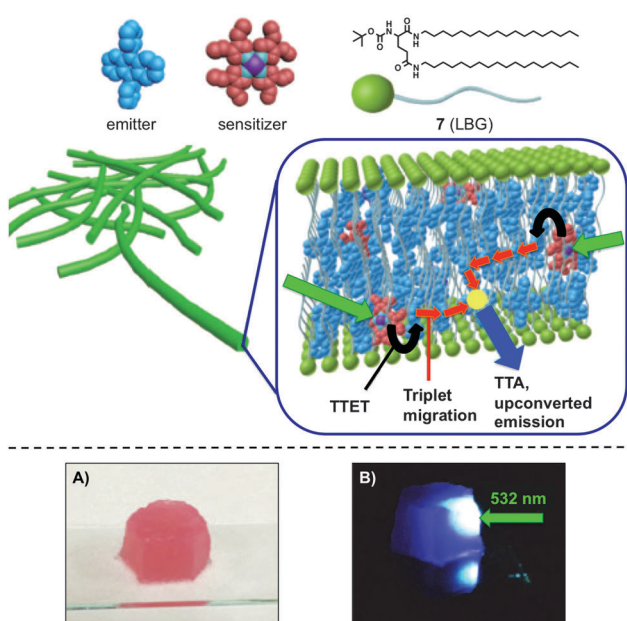




**Scheme 6** Photograph of a glass slide spin-coated with PUC organogel (top) and partial zoom (bottom). The slide was submersed in an oxygen-scavenging water layer. When 532 nm light is applied to slide, PUC is clearly visible along the path of the laser in the region covered by the film (surrounded by the black dashed line, bottom). When a patch of the gel layer was removed (dotted white outline, bottom), UC light was not visible in that region. Adapted with permission from ref. 32. Copyright © 2015 American Chemical Society.

have confirmed the identical TTA-UC efficiency in the quasi-solid gelated sample and in a comparable liquid composition ( $\Phi_{\text{TTA}} = 0.07$ ). As a matter of fact, this finding emerges as a suitable strategy for potential applications in devices where the gel matrix needs to be processed as a thin film (Scheme 6), photovoltaics, and photocatalytic water splitting.

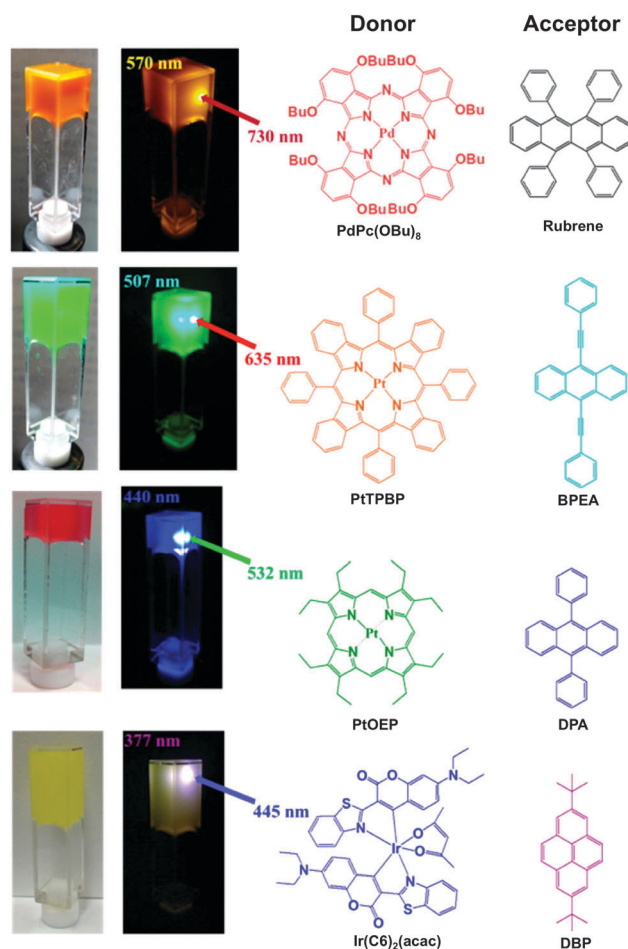
Moreover, an efficient TTA-UC process was also recently developed using supramolecular organogel matrices based on *N,N'*-bis(octadecyl)-L-boc-glutamic diamide (7) as LMW gelator (Scheme 7).<sup>33</sup> In this case, intense UC emission was detected



**Scheme 7** Schematic representation of the structural unit of the upconversion ternary gel system (top), and pictures of the gel shaped in a mould under (A) white light and (B) 532 nm green laser (bottom). Adapted with permission from ref. 33. Copyright © 2015 American Chemical Society.

from different donor (sensitizer)-acceptor (emitter) pairs in organogels made of 7 even under air-saturated condition, which undoubtedly represents a major achievement in this emerging field.

These TTA-UC molecular systems were formed by spontaneous accumulation of donor and acceptor molecules in the gel nanofibers, which were apparently stabilized by developed hydrogen bonded networks. These molecules, pre-organized in the gel network, showed efficient transfer and migration of triplet energy, as revealed by a series of spectroscopic, microscopic, and rheological characterizations. Interestingly, efficient TTA-UC was achieved even under excitation power lower than the solar irradiance. These observations reveal the adaptive feature of host fibrillar gel networks that allowed efficient and cooperative inclusion of donor-acceptor molecules while maintaining their supramolecular structural integrity. Moreover, the air-stable TTA-UC in the supramolecular gel was observed for a wide combination of donor-acceptor pairs, which enabled efficient near IR-to yellow, red-to-cyan, green-to-blue, and blue-to-UV wavelength conversions (Scheme 8).



**Scheme 8** Photographs of ternary UC gels in air-saturated DMF before and after irradiation. Short pass filters were used to remove the scattered excitation lights. Chemical structures of donor and acceptor pairs used in this work are also shown. Adapted with permission from ref. 33. Copyright © 2015 American Chemical Society.

## Intragel photochemical reactivity

The use of gel networks as confined systems to influence the course of organic photo-induced reactions has been practically unexplored and only few examples can be found in the recent literature. These reports include either photodimerization or photooxidation processes or are discussed next.

### Photodimerization

Although anthracene photodimerization is one of the oldest known photochemical reactions, it still remains one of the most studied processes in different hosts or template molecules. In this respect, Shinkai and co-workers reported the first example in which a binary gelator containing a 2-anthracenecarboxylic acid (2Ac) was investigated, resulting in a very high degree of stereoselectivity under simple conditions.<sup>34</sup> Subsequently, they developed a new class of binary organogelator based on 2Ac, attached non-covalently with the gelator counterpart containing a 3,4,5-tris(*n*-dodecyloxy)-benzoylamide backbone.<sup>35</sup> Different degrees of stereoselectivity for different systems were observed when 2Ac-containing gel samples were irradiated. Furthermore, the nature of both gelator and solvent was found to play an important role in the stereochemistry of the obtained photodimers. Ongoing with this research, the same group demonstrated that a high degree of chiral induction could be also achieved and controlled precisely by the 1D supramolecular gelator assembly, which would path the way for future research in this direction.<sup>36</sup>

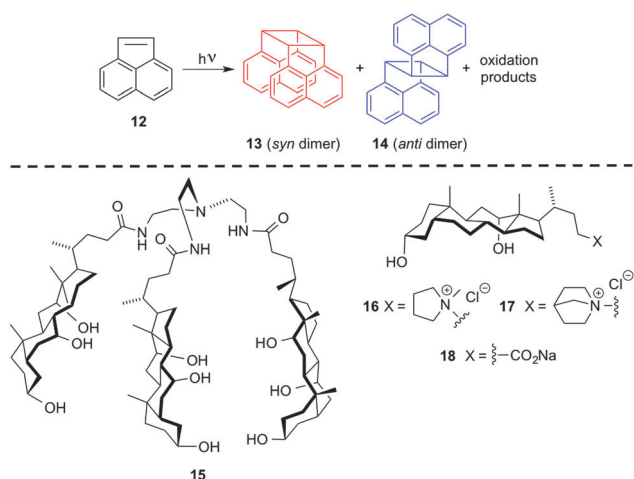
Although photodimerization of acenaphthylene (**8**) (Scheme 9, top), which usually yields a mixture of *syn* (**9**) and *anti* (**10**) dimers along with minor oxidation products, had been previously studied in confined media such as zeolites or micellar solutions. However, Maitra and co-workers investigated the process, for the first time, inside supramolecular hydrogels (*i.e.*, based on LMW bile acids **11–14**, Scheme 9, bottom) as potential photochemical nano-reactors.<sup>37</sup> The results showed that the photodimer ratio (**9** : **10**) obtained for the reaction performed in the gel-bound phase

was 3–10 higher in comparison to either micellar solutions or water. Very remarkably, the product selectivity was found to be highly dependent on the rheological properties of the hydrogels, obtaining higher storage modulus ( $G'$ ) in the most rigid gels (*i.e.*, **13** > **12** > **14** > **11**). Fluorescence experiments showed different intensity of the ACN-excimer band in the gel-bound state and in micellar solution, pointing out the existence and a key role of different molecular interactions patterns during the photochemical process.

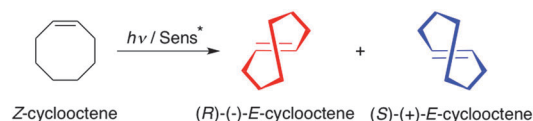
More recently, Yadav and co-workers<sup>38</sup> have also reported the use of an organogel (*i.e.*, made from enantiomerically pure 3,4-*O*-isopropylidene- $\alpha$ -D-arabinose) as a reaction vessel for the production of a bicyclo[3.2.1]octanone *via* photo-induced electron transfer (PET) upon irradiation at 300 nm. Both yield and reaction time were similar to those obtained in solution state.<sup>39</sup> Importantly from the recycling point of view, the gelator could be also recovered from the mixture after column chromatography.

### Photosensitized isomerization

Yang, Trotta, Inoue and co-workers<sup>40</sup> have recently reported the preparation of hydrogels made of polymers based on cyclic nigerosyl-nigerose (CNN; a saucer-shaped tetrasaccharide) that act as a “nanosponge” (NS). The CNN-NSs were prepared by cross-linking CNN with pyromellitic dianhydride (PDA) at different ratios. These polymeric materials effectively worked as chiral supramolecular sensitizers (Sens\* in Scheme 10, bottom) and mediated the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene to chiral (*E*)-isomer (Scheme 10, top). Note that CNN is a “pseudo” host lacking a confining cavity to fully accommodate the guest molecule. Very interestingly, the product's ee was dramatically controlled by the phase evolved. Indeed, the ee of the (*E*)-isomer was low in solution and suspension, but rapidly increased at the



**Scheme 9** Photodimerization reaction of acenaphthylene (**8**) (top) and structure of hydrogelators **11–14** (bottom).<sup>37</sup>



**Scheme 10** Enantiodifferentiating photoisomerization of (*Z*)-cyclooctene to chiral (*E*)-cyclooctene (top) mediated by CNN-NSs (bottom).<sup>40</sup>

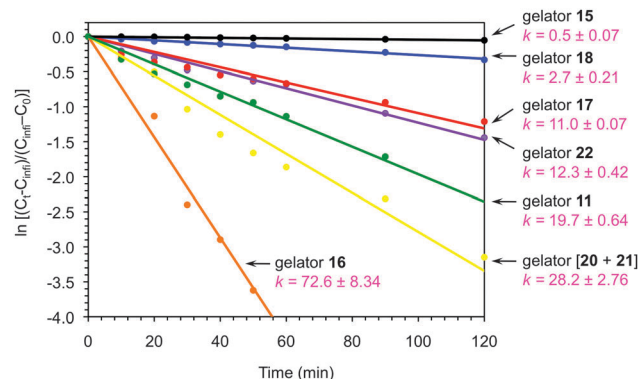




phase border between flowing gel and rigid gel. These results are very stimulating because they clearly reveal the beneficial role of the chiral void space formed upon gelation of the crosslinked polysaccharide on the outcome (*i.e.*, chirality transfer) of supramolecular photochirogenic reactions. The methodology seems to be applicable to other substrates and reactions by choosing appropriate sensitizing crosslinkers and chiral building blocks.

### Photooxidation

Díaz and co-workers established the potential of a various soft gels as nanoreactors for a model photocatalytic reaction (Scheme 11).<sup>41</sup> Specifically, riboflavin tetracetate (**25**)-catalyzed aerobic photooxidation of 1-(4-methoxyphenyl)ethanol (**23**) was investigated as a model reaction under blue visible light in gels made from either high or LMW compounds (**11**, **14–22**). Three strategies involving different degrees of organization of the photocatalyst within the gel network were explored, and the results were compared to those obtained in homogeneous and micellar solutions. In general, physical entrapment of both the catalyst and the substrate under optimized concentrations into the gels allowed the photooxidation with conversions between 55 and 100% within 120 min (TOF  $\sim$  0.045–0.08 min<sup>−1</sup>;  $k \sim$  0.011–0.028 min<sup>−1</sup>), albeit with first-order rates *ca.* 1–3-fold lower than in solution under comparable non-stirred conditions. Surprisingly, the organogel



**Scheme 12** Selection of first-order kinetics plots of RFT-catalyzed photooxidation of **23** in gel media prepared with different gelators. Solvent systems: H<sub>2</sub>O (gelators **17**, **22**, [**20** + **21**]; 1 : 1 w/w); H<sub>2</sub>O + DMSO (95 : 5 v/v) (gelator **18**); 0.5 M NaCl (gelator **15**); H<sub>2</sub>O + AcOH (80 : 20 v/v) (gelator **11**); CH<sub>3</sub>CN (gelator **16**). Estimated rate constants ( $\times 10^3$  min<sup>−1</sup>),  $k$ , are given for each case. Adapted with permission from ref. 41. Copyright © 2013 Royal Chemical Society.

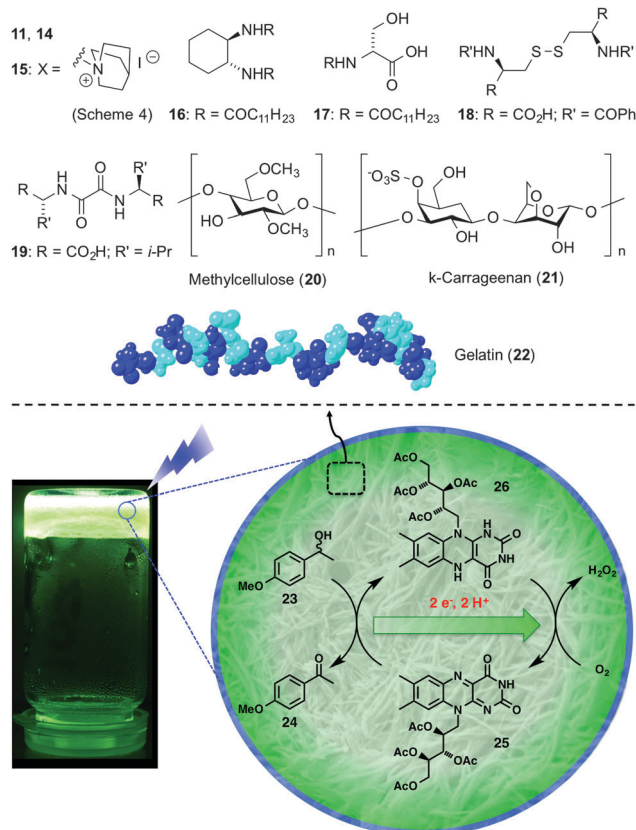
made in CH<sub>3</sub>CN using the cyclohexane-based bisamide gelator **16** not only stabilized the catalyst against photodegradation but also afforded full conversion in less than 60 min (TOF  $\sim$  0.167 min<sup>−1</sup>;  $k \sim$  0.073 min<sup>−1</sup>) without the need of additional proton transfer mediators (*e.g.*, thiourea) as it occurs in CH<sub>3</sub>CN solutions.

It is important to mention that the gelators could be recycled and reused in further runs without detriment to their gelation ability and reaction rates. Moreover, the kinetics of the photocatalytic process could be fine-tuned according to the properties of the gel media (Scheme 12). For example, entangled fibrillar networks with relatively high mechanical strength, as determined by scanning electron microscopy (SEM) and rheological measurements, were usually connected to lower reaction rates, whereas wrinkled laminated morphologies seemed to favor the reaction. In addition, the kinetic results showed in most cases a good correlation with the aeration efficiency of the gel media.<sup>41</sup>

## Conclusions and outlook

Inspired by the efficiency of self-organizing compartmentation in natural systems to drive challenging transformations, research on photo-induced processes carried out inside gel matrices represents a growing and highly active new area (*i.e.*, involving embedded reactants that do not participate directly in the assembly of the gel network). One of the advantages of photochemical processes for such studies is that it can be triggered without any thermal shock, which could disrupt the organization of the self-assembled fibrillar gel network. On the other hand, large active surface areas, good diffusion properties, variety of compositions, simple preparation from readily available molecular building blocks, very low concentration of gelator molecules, and the reversible stimuli-responsive nature of many self-assembled gels, make them ideal systems to mimic more complex natural systems.

A few initial studies on the rate of electron transfer photo-reactions inside gels have provided the background for more



**Scheme 11** Gelators (**11**, **14–22**) (top) and riboflavin tetracetate-catalysed photooxidation of 1-(4-methoxymethyl)ethanol (**23**) inside gel media using blue visible light (bottom). Adapted with permission from ref. 41. Copyright © 2013 Royal Chemical Society.

demanding photophysical processes such as photon UC based on triplet-triplet annihilation (TTA-UC). Moreover, additional examples have demonstrated the feasibility of soft gels as reaction vessels and nanoreactors for photochemical processes such as photodimerizations, photosensitized isomerization, and photooxidations. Herein, the efforts are oriented towards the fabrication of spatially confined micro- and nanoreactors to improve kinetics, selectivity and/or processability in comparison to homogeneous solutions. Thus, important fields such as photovoltaics, photocatalysis and phototherapy will undoubtedly be great beneficiaries of future developments with respect to intragel photo-induced processes as well as the use of triple excited states as reporters.

Furthermore, a number of fundamental studies will still be necessary in future work in order to establish the real scope and boost the applicability of these materials as reaction vessels and nanoreactors for photo-induced processes. Those may include, among others, the following:

(a) The elucidation of different molecular interactions between the fibrillar network and the reactants that may play a key role in photo-induced processes. This will also shed light on the organization mode of reactants within the gel matrix,

(b) the correlation between gel properties (*i.e.*, morphological, mechanical, diffusion, and thermodynamic properties) and the outcome of the photoreaction,

(c) the development of reliable strategies to improve the loading capacity of the gel (*i.e.*, concentration of reactants) networks and their robustness for higher operational stability, while retaining their functional properties,

(d) the determination of optimal specificity and strength absorption of substrates in the gel matrix as well as the evaluation of possible concentration effects, and

(e) the fundamental understanding of mechanisms through which self-assembled gels may favor specific reaction pathways (*e.g.*, steric interactions that could control spatial orientation of specific reactants and influence reaction selectivity, accumulation of reactants into nanostructured subdomains creating “hot-spots” of catalytic activity).

## Acknowledgements

R.P.R thanks the financial support from the IEF Marie Curie program of the European Union (PIEF-GA-2013-625064). D.D.D. thanks the DFG for the Heisenberg professorship award (PRJ 9209720).

## Notes and references

- 1 M. Vriezema, M. C. Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan and R. J. M. Nolte, *Chem. Rev.*, 2005, **105**, 1445–1489.
- 2 Z. V. Todres, *Organic chemistry in confined media*, Springer International Publishing, Switzerland, 2013.
- 3 G. Palmisano, V. Augugliaro, M. Pagliaro and L. Palmisano, *Chem. Commun.*, 2007, 3425–3437.
- 4 D. G. Shchukin and D. V. Sviridov, *J. Photochem. Photobiol., C*, 2006, **7**, 23–39.
- 5 M. D. Ward, *Chem. Soc. Rev.*, 1997, **26**, 365–375.
- 6 A. Maldotti, A. Molinari and R. Amadelli, *Chem. Rev.*, 2002, **102**, 3811–3836.
- 7 M. Pagliaro, R. Ciriminna and G. Palmisano, *Chem. Soc. Rev.*, 2007, **36**, 932–940.
- 8 M. Antonietti and G. A. Ozin, *Chem. – Eur. J.*, 2004, **10**, 28–41.
- 9 J. H. Fendler, *Chem. Rev.*, 1987, **87**, 877–899.
- 10 J. G. Riess, *Chem. Rev.*, 2001, **101**, 2797–2920.
- 11 C. Harris and P. V. Kamat, *ACS Nano*, 2009, **3**, 682–690.
- 12 O. V. Vasil'tsova and V. N. Parmon, *Kinet. Catal.*, 1999, **40**, 62–70.
- 13 K. Uekama, F. Hirayama and T. Irie, *Chem. Rev.*, 1998, **98**, 2045–2076.
- 14 D. G. Shchukin, E. A. Ustinovich, A. I. Kulak and D. V. Sviridov, *Photochem. Photobiol. Sci.*, 2004, **3**, 157–159.
- 15 D. K. Smith, in *Supramolecular Chemistry From Molecules to Nanomaterials*, ed. J. W. Steed and A. P. Gale, Wiley & Sons Ltd., Chichester, UK, 1st edn, 2012, vol. 7, pp. 3355–3376.
- 16 D. D. Díaz, D. Kühbeck and R. J. Koppmans, *Chem. Soc. Rev.*, 2011, **40**, 427–448.
- 17 G. Perot and M. Guisnet, *J. Mol. Catal.*, 1990, **61**, 173–196.
- 18 M. N. Khan, *Micellar catalysis*, Surfactant science series, Boca Raton (FL), USA, CRC Press, 2007, vol. 133.
- 19 R. T. Cheriya, A. R. Mallia and M. Hariharan, *Energy Environ. Sci.*, 2014, **7**, 1661–1669.
- 20 A. Del Guerzo and J.-L. Pozzo, in *Molecular Gels. Materials with Self-Assembled Fibrillar Networks*, ed. P. Terech and G. Weiss, Kluwer Academic, New York, USA, 2005, pp. 813–851.
- 21 A. Shumburo and M. C. Biewer, *Chem. Mater.*, 2002, **14**, 3745–3750.
- 22 F. Galindo, M. I. Burguete, R. Gavara and S. V. Luis, *J. Photochem. Photobiol., A*, 2006, **178**, 57–61.
- 23 M. I. Burguete, M. A. Izquierdo, F. Galindo and S. V. Luis, *Chem. Phys. Lett.*, 2008, **460**, 503–506.
- 24 P. D. Wadhavane, R. E. Galian, M. A. Izquierdo, J. Aguilera-Sigalat, F. Galindo, L. Schmidt, M. Isabel Burguete, J. Pérez-Prieto and S. V. Luis, *J. Am. Chem. Soc.*, 2012, **134**, 20554–20563.
- 25 P. D. Wadhavane, M. A. Izquierdo, F. Galindo, M. I. Burguete and S. V. Luis, *Soft Matter*, 2012, **8**, 4373–4381.
- 26 T. N. Singh-Rachford and F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560–2573.
- 27 J. Z. Zhao, S. M. Ji and H. M. Guo, *RSC Adv.*, 2011, **1**, 937–950.
- 28 J. H. Kim and J. H. Kim, *J. Am. Chem. Soc.*, 2012, **134**, 17478–17481.
- 29 A. Monguzzi, R. Tubino, S. Hoseinkhani, M. Campione and F. Meinardi, *Phys. Chem. Chem. Phys.*, 2012, **14**, 4322–4332.
- 30 V. Gray, D. Dzebo, M. Abrahamsson, B. Albinsson and K. Moth-Poulsen, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10345–10352.
- 31 R. Vadrucchi, C. Weder and Y. C. Simon, *Mater. Horiz.*, 2015, **2**, 120–124.



- 32 K. Sripathy, R. W. MacQueen, J. R. Peterson, Y. Y. Cheng, M. Dvořák, D. R. McCamey, N. D. Treat, N. Stingelind and T. W. Schmidt, *J. Mater. Chem. C*, 2015, **3**, 616–622.
- 33 P. Duan, N. Yanai, H. Nagatomi and N. Kimizuka, *J. Am. Chem. Soc.*, 2015, **137**, 1887–1894.
- 34 A. Dawn, N. Fujita, S. Haraguchi, K. Sada and S. Shinkai, *Chem. Commun.*, 2009, 2100–2102.
- 35 A. Dawn, N. Fujita, S. Haraguchi, K. Sada, S.-i. Tamaru and S. Shinkai, *Org. Biomol. Chem.*, 2009, **7**, 4378–4385.
- 36 A. Dawn, T. Shiraki, S. Haraguchi, H. Sato, K. Sada and S. Shinkai, *Chem. – Eur. J.*, 2010, **16**, 3676–3689.
- 37 S. Bhat and U. Maitra, *Molecules*, 2007, **12**, 2181–2189.
- 38 Rajkamal, D. Chatterjee, A. Paul, S. Banerjee and S. Yadav, *Chem. Commun.*, 2014, **50**, 12131–12134.
- 39 S. Yadav, S. Banerjee, D. Maji and S. Lahiri, *Tetrahedron*, 2007, **63**, 10979–10990.
- 40 X. Wei, W. Liang, W. Wu, C. Yang, F. Trotta, F. Caldera, A. Mele, T. Nishimoto and Y. Inoue, *Org. Biomol. Chem.*, 2015, **13**, 2905–2912.
- 41 J. Bachl, A. Hohenleutner, B. B. Dhar, C. Cativiela, U. Maitra, B. König and D. D. Díaz, *J. Mater. Chem. A*, 2013, **1**, 4577–4588.

